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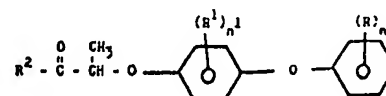
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(54) Phenoxyphenoxypropionic acid derivatives, process for their preparation, herbicidal compositions containing them and a method of controlling weeds using them

(57) R-isomers of compounds of the general formula



in which n and n' independently represents 0 or an integer of 1 to 3; each R independently represents a halogen atom, a methoxy group or an alkyl group having 1 to 4 carbon atoms; each R¹ independently represents a halogen atom or a methyl group; and R² represents a group of the general formula OR³, SR⁴, NHR⁵ or NR⁶R⁷, in which R³ represents one equivalent of a salt-forming cation, a hydrogen atom, an alkyl group having from 1 to 10 carbon atoms, a trichloroethyl group, an alkenyl group having from 2 to 4 carbon atoms, a cyclohexyl group optionally substituted by one or more methyl groups, a cyclopentyl group, a phenyl group optionally substituted by one or two halogen atoms, or a benzyl group; R⁴ represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group optionally substituted by one or two halogen atoms, or a benzyl group; R⁵ represents a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms, a phenyl group optionally substituted by one or more substituents selected from halogen atoms and -CF₃, -OCF₂CF₂H and -CO₂CH₃ groups, or a benzyl group; R⁶ represents an alkyl or alkoxy group having from 1 to 4 carbon atoms; have useful selective herbicidal properties, especially against grass-like weeds in barley.

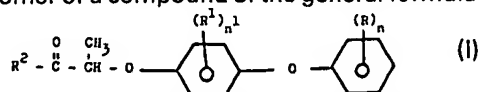
SPECIFICATION

Phenoxyphenoxypropionic acid derivatives, process for their preparation, herbicidal compositions containing them and a method of controlling weeds using them

5 The present invention relates to phenoxyphenoxypropionic acid derivatives, process for their preparation, herbicidal compositions containing them and a method of controlling weeds using them. 5

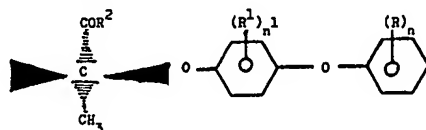
It has been disclosed that certain 4-phenoxyphenoxy- α -propionic acid derivatives have an excellent selective herbicidal effect against weed grasses in crop plants. The Applicants have now found that certain 10 single optical isomers of these compounds exhibit a much greater herbicidal effect against grass weeds than do the racemic mixtures. Moreover, most surprisingly, the phytotoxic effects of these single isomers against crop plants are not significantly greater than the effects of the racemic mixtures. The single optical isomers have therefore a significantly improved selectivity between grass weeds and crop plants, compared with the racemic mixtures. 10

15 The invention provides the R-isomer of a compound of the general formula 15



in which n represents 0 or an integer of 1 to 3; n^1 represents 0 or an integer of 1 to 3; each R independently 20 represents a halogen atom, a methoxy group or an alkyl group having 1 to 4 carbon atoms; each R^1 independently represents a halogen atom or a methyl group; and R^2 represents a group of the general formula OR^3 , SR^4 , NHR^5 or NR^6R^7 , in which R^3 represents one equivalent of a salt-forming cation, a hydrogen atom, an alkyl group having from 1 to 10 carbon atoms, a trichloroethyl group, an alkenyl group having from 2 to 4 carbon atoms, a cyclohexyl group optionally substituted by one or more methyl groups, a cyclopentyl 25 group, a phenyl group optionally substituted by one or two halogen atoms, or a benzyl group; R^4 represents an alkyl group having from 1 to 6 carbon atoms, a phenyl group optionally substituted by one or two halogen atoms, or a benzyl group; R^5 represents a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms, a phenyl group optionally substituted by one or more substituents selected from halogen atoms and $-CF_3$, $-OCF_2CF_2H$ and $-CO_2CH_3$ groups, or a benzyl group; R^6 represents an alkyl group having from 1 to 4 carbon 30 atoms; and R^7 represents an alkyl or alkoxy group having from 1 to 4 carbon atoms. 30

The R-isomer of a compound of the general formula I is the isomer whose absolute configuration is:

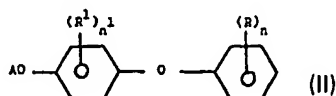


Preferably any halogen atom present in a compound of the general formula I is a chlorine atom, and preferably any alkyl moiety has from 1 to 4 carbon atoms. If R^3 represents an alkenyl group this is preferably 40 an allyl group. Preferred salts -i.e. those compounds of the general formula I in which R^3 represents one equivalent of a salt-forming cation - are alkali metal, especially sodium and potassium, salts. 40

Preferably n^1 represents 0. Preferably n represents 1 or 2 and the or each R represents a halogen atom, especially a chlorine atom. Preferably, R^2 represents a group of formula OR^3 wherein R^3 represents an alkyl group, especially an alkyl group having from 1 to 4 carbon atoms, for example a methyl or an isobutyl group. 45 R-(methyl 2-[4-(2,4-dichlorophenoxy)phenoxy]propionate) and R-(isobutyl 2-[4-(4-chlorophenoxy)phenoxy]propionate) have been found to have especially useful properties and are therefore the most preferred isomers of the invention. 45

The R-isomers according to the invention may be prepared by the resolution of racemic mixtures of compounds of the general formula I by methods analogous to methods known in the art, for example by 50 chromatography on an optically active column, or by reaction with an optically active reagent, subsequent separation of the resulting geometric isomers and regeneration of the compound of the formula I. 50

Preferably, however, an R-isomer according to the invention is prepared by the coupling of two compounds, one of which is in the form of a single optical isomer. For example, an R-isomer according to the invention may be prepared by reacting a compound of the general formula: 55



60 wherein R, R^1 , n and n^1 have the meanings given for the general formula I, and A represents a hydrogen atom or an alkali metal ion, with the S-isomer of a compound of the general formula: 60



wherein R^2 has the meaning given for the general formula I and the group X is a suitable leaving group, the reaction being carried out in the presence of a base if A represents a hydrogen atom; and if desired, subsequently converting the resulting R-isomer of a compound of the general formula I into the R-isomer of another compound of the general formula I by any suitable method.

5 The S-isomer of a compound of the general formula III has the absolute configuration



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15 The coupling reaction between the compounds of the formulae II and III proceeds with inversion of the optical configuration of the asymmetric carbon atom in the compound of formula III. It is of course important that the reaction conditions should be such that no racemisation of the compound of the general formula III or the resulting compound of the general formula I takes place during the reaction.

The leaving group X may for example be a group of the general formula $-O.SO_2.Q$ or $-O.CO.Q$, wherein Q is a hydrocarbonyl group, for example an alkyl or aryl group having up to 10 carbon atoms; a group of the general formula $-O.CH(OH).CHAl_3$, wherein each Hal is a halogen atom, suitably a chlorine, fluorine or bromine atom; or a halogen atom, preferably a chlorine atom. Preferably the leaving group X is an $-O.SO_2.Q$ group, especially a methanesulphonyl group or a para-toluenesulphonyl group.

25 If A represents a hydrogen atom in the compound of the general formula II, the reaction according to the invention must be carried out in the presence of a base. This base must be selected so that racemisation does not take place. Preferably the base is inorganic; it may for example be an alkali metal carbonate or bicarbonate, for example sodium carbonate, or an alkali metal alkoxide, for example sodium methoxide. If A represents an alkali metal ion, the compound of the general formula II may be prepared from the corresponding free phenol by reaction with a base, for example an alkali metal alkoxide, for example sodium methoxide.

30 The coupling reaction between the compounds of the formulae II and III is suitably carried out at elevated temperature, preferably at a temperature in the range 50 to 200°C. Generally, reactions in which A represents a hydrogen atom require a somewhat higher temperature than reactions in which the starting material is a pre-formed alkali metal phenolic salt. If A represents an alkali metal ion, the reaction temperature is preferably in the range 70 to 100°C; if A represents a hydrogen atom, the reaction temperature is preferably in the range 110 to 170°C.

If one of the reactants is a liquid at the reaction temperature, the reaction may be performed without an added solvent. However, a suitable solvent, for example an optionally-substituted aromatic compound, preferably a hydrocarbon, such as toluene or xylene, may be used.

40 The S-isomer of a compound of the general formula III used as starting material for the coupling reaction may be prepared by replacing the $-OH$ group marked * in an S-isomer of a compound of the general formula:



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50 wherein R^2 has the meaning given for the general formula I, with the leaving group X, under reaction conditions such that racemisation does not take place. This replacement may for example be carried out by reacting a compound of the general formula IV with thionyl chloride and decomposing the resultant compound to give a compound of the general formula III in which X represents a chlorine atom; by esterifying the $-OH$ group in a compound of the general formula IV using for example an acid halide or an acid anhydride to produce a compound of the general formula III in which X represents an $-O.SO_2.Q$ or $-O.CO.Q$ group; or reacting a compound of the general formula IV with a halogenated aldehyde of general formula $CHAl_3.CHO$, to produce a compound of the general formula III in which X represents an $-O.CH(OH).CHAl_3$ group.

60 The S-isomer of a compound of the general formula IV has the absolute configuration:



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formula I and subsequently convert this isomer into the R-isomer of another compound of the general formula I. For example, it may be desirable to use S-(+)-lactic acid - i.e. the compound of the general formula IV wherein R² represents a hydrogen atom - as starting material due to its ready availability, and subsequently to esterify the resultant compound of the general formula I by conventional techniques to form a compound of the general formula I in which R² represents an alkoxy group.

The R-isomers according to the invention have a highly selective herbicidal activity against grass-like weeds, including wild oats, in cereal crops, such as wheat and, especially, barley. The R-isomer is preferably used as a herbicide in the form of a herbicidal composition. The invention therefore also provides a herbicidal composition which comprises an R-isomer according to the invention together with a carrier. A mixture of two or more carriers may be used.

The invention further provides a method of selectively combating grass-like weeds in cereal crops, especially barley, which comprises applying to the crop area an R-isomer according to the invention or a herbicidal composition according to the invention.

Throughout this Specification, "cereal crops" should of course be understood to mean crops other than oats.

A carrier in a composition according to the invention is any material with which the active ingredient is formulated to facilitate application to the locus to be treated, which may for example be a plant, seed or soil, or to facilitate storage, transport or handling. A carrier may be a solid or a liquid, including a material which is normally gaseous but which has been compressed to form a liquid, and any of the carriers normally used in formulating herbicidal compositions may be used.

Suitable solid carriers include natural and synthetic clays and silicates, for example natural silicas such as diatomaceous earths; magnesium silicates, for example talcs; magnesium aluminium silicates, for example attapulgites and vermiculites; aluminium silicates, for example kaolinities, montmorillonites and micas; calcium carbonate; calcium sulphate; synthetic hydrated silicon oxides and synthetic calcium or aluminium silicates; elements, for example carbon and sulphur; natural and synthetic resins, for example coumarone resins, polyvinyl chloride, and styrene polymers and copolymers; solid polychlorophenols; bitumen; waxes, for example beeswax, paraffin wax, and chlorinated mineral waxes; and solid fertilisers, for example superphosphates.

Suitable liquid carriers include water; alcohols, for example isopropanol and glycols; ketones, for example acetone, methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone; ethers; aromatic or aliphatic hydrocarbons, for example benzene, toluene and xylene; petroleum fractions, for example kerosine and light mineral oils; chlorinated hydrocarbons, for example carbon tetrachloride, perchlorethylene and trichloroethane. Mixtures of different liquids are often suitable.

Herbicidal compositions are often formulated and transported in a concentrated form which is subsequently diluted by the user before application. The presence of small amounts of a carrier which is a surface-active agent facilitates this process of dilution. Thus preferably at least one carrier in a composition according to the invention is a surface-active agent;

A surface-active agent may be an emulsifying agent, a dispersing agent or a wetting agent; it may be nonionic or ionic. Examples of suitable surface-active agents include the sodium or calcium salts of polyacrylic acids and lignin sulphonic acids; the condensation products of fatty acids or aliphatic amines or amides containing at least 12 carbon atoms in the molecule with ethylene oxide and/or propylene oxide; fatty acid esters of glycerol, sorbitan, sucrose or pentaerythritol; condensates of these with ethylene oxide and/or propylene oxide; condensation products of fatty alcohol or alkyl phenols, for example *p*-octylphenol or *p*-octylcresol, with ethylene oxide and/or propylene oxide; sulphates or sulphonates of these condensation products; alkali or alkaline earth metal salts, preferably sodium salts, of sulphuric or sulphonic acid esters containing at least 10 carbon atoms in the molecule, for example sodium lauryl sulphate, sodium secondary alkyl sulphates, sodium salts of sulphonated castor oil, and sodium alkylaryl sulphonates such as sodium dodecylbenzene sulphonate; and polymers of ethylene oxide and copolymers of ethylene oxide and propylene oxide.

The compositions of the invention may for example be formulated as wettable powders, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates and aerosols. Wettable powders usually contain 25, 50 and 75% w of active ingredient and usually contain, in addition to solid inert carrier, 3-10% w of a dispersing agent and, where necessary, 0.10% w of stabiliser(s) and/or other additives such as penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and are diluted in the field with further solid carrier to give a composition usually containing 1/2 - 10% w of active ingredient. Granules are usually prepared to have a size between 10 and 100 BS mesh (1.676 - 0.152 mm), and may be manufactured by agglomeration or impregnation techniques. Generally, granules will contain 1/2 - 25% w active ingredient and 0 - 10% w of additives such as stabilisers, slow release modifiers and binding agents. Emulsifiable concentrates usually contain, in addition to a solvent and, when necessary, co-solvent, 10 - 50% w/v active ingredient, 2 - 20% w/v emulsifiers and 0 - 20% w/v of other additives such as stabilizers, penetrants and corrosion inhibitors. Suspension concentrates are usually compounded so as to obtain a stable, non-sedimenting flowable product and usually contain 10 - 75% w active ingredient, 0.5 - 15% w of dispersing agents, 0.1 - 10% w of

the active ingredient is substantially insoluble; certain organic solids or inorganic salts may be present dissolved in the formulation to assist in preventing sedimentation or as antifreeze agents for water.

Aqueous dispersions and emulsions, for example compositions obtained by diluting a wettable powder or a concentrate according to the invention with water, also lie within the scope of the present invention. The said emulsions may be of the water-in-oil or of the oil-in-water type, and may have a thick 'mayonnaise'-like consistency.

The compositions of the invention may also contain other ingredients, for example, other compounds possessing pesticidal, herbicidal or fungicidal properties.

The following Examples illustrate the invention.

10 EXAMPLE 1 10

Synthesis of R-(+)-(methyl 2-[4-(2,4-dichlorophenoxy)phenoxy]propionate)

4-(2,4-dichlorophenoxy)phenol (5.10 g, 2.0×10^{-2} mol), S-(−)-ethyl lactate mesylate ($\alpha_D^{25} = -70.17^\circ$ (neat)) (3.64 g, 2.0×10^{-2} mol) and Na_2CO_3 (1.16 g, 1.1×10^{-2} mol) were heated at 150° for 8.5 hours. The conversion to products was measured by gas chromatography as being 40%, 71% and 87% after 1, 4 and 8.25 hours respectively. 15

The mixture was then treated with toluene (25 ml), and then washed with water, 2M NaOH, and water to neutrality. The mixture was dried azeotropically to give R-(+)-(methyl 2-[4-(2,4-dichlorophenoxy)phenoxy]propionate) as an oil (4.92 g, corresponding to a yield of 72%). The optical rotation α_D^{23} of a 2% by weight solution of the product in ethanol was $+24.7^\circ$. The structure of the product was confirmed using NMR and IR spectroscopy and elemental analysis. 20

EXAMPLE 2

Preparation of R-isobutyl(2-[4-chlorophenoxy]phenoxy)propionate

4-(4-chlorophenoxy)phenol (6.61 g, 0.03 mole), potassium hydroxide (1.68 g, 0.03 mole) and ethanol were refluxed for 1 hour. The solution was evaporated to about 50 ml bulk and toluene (500 ml) was added and the mixture distilled until the temperature was 110°C . At this time a fine solid suspension had separated from the stirred refluxing solution. S-isobutyl lactate mesylate (6.72 g, 0.03 mole) was added dropwise over 1 hour and the mixture stirred and refluxed for 18 hours. The mixture was washed with water and the toluene layer evaporated to give a brown oil which was distilled under reduced pressure to produce the desired compound. 25

The first fraction, boiling at $178 - 180^\circ\text{C}$ at 0.25 mmHg pressure, had an optical rotation $\alpha_D^{25} = +18.896^\circ$, and the second fraction, boiling at $180 - 182^\circ\text{C}$ at 0.25 mmHg pressure, had an optical rotation $\alpha_D^{25} = +22.489^\circ$. Crystals settled out from these fractions on standing, and the supernatant oils had the following rotations: 30

First Fraction : α_D^{25} : 26.0°
Second fraction : α_D^{25} : 31.0° 35

40 EXAMPLE 3 40

Selective herbicidal activity of R-(+)-(methyl[4-(2,4-dichlorophenoxy)phenoxy]propionate)

The test active ingredients in this Example were the racemic mixture R,S-(±)-(methyl[4-(2,4-dichlorophenoxy)phenoxy]propionate) and the single isomer R-(+)-(methyl[4-(2,4-dichlorophenoxy)phenoxy]propionate) and the test plants were barley, *Hordeum vulgare*, and cultivated oats, *Avena sativa*; cultivated oat, *Avena sativa*, was used as a test species rather than wild oat, *Avena fatua*, since *Avena sativa* is more easy to grow and to test; experience has shown that results obtained using *Avena sativa* are also applicable to *Avena fatua*. 45

The test active ingredients were made up into emulsifiable concentrates containing 20% weight active ingredient, 10% weight of a mineral oil, emulsifiers, and xylene as solvent.

Each concentrate was diluted with water and test plants were sprayed at various doses corresponding to the following: 50

oat *Avena sativa*

Racemate applied at 3.0, 1.0 and 0.3 kg/hectare

R-isomer applied at 1.5, 0.5 and 0.15 kg/hectare

barley *Hordeum vulgare* 55

Racemate applied at 4.0, 2.0 and 0.4 kg/hectare

R-isomer applied at 2.0, 0.6 and 0.2 kg/hectare

4 replicates were used at each dosage. After 14 days, the effects of the active ingredients were assessed visually, for barley on a 0-9 scale in which 0 indicates no damage and 9 indicates death of the plant, and for oats on a 0-100 scale in which 0 indicates growth as in the untreated control plants and 100 indicates no visible growth after treatment. 60

After 22 days, the fresh weights of the barley plants were measured relative to the untreated controls and after 36 days fresh weights of the oat plants were measured relative to the untreated controls.

and b in a relationship of the form:-

$$\text{Probit (\% response)} = a + b \log (\text{dosage})$$

Using the resultant curve, dosages corresponding to a given level of response can be calculated. In this Example, a GID_{50} , that is, the dosage required to produce a 50% response to the active ingredient, was calculated for each species, as shown in Table 1. Table 1 also shows the relative selectivity of each active ingredient between oats and barley.

TABLE 1

Active Ingredient	Oats GID_{50} (Kg/ha)	Barley GID_{50} (Kg/ha)	Selectivity $\frac{\text{GID}_{50} \text{ Barley}}{\text{GID}_{50} \text{ Oats}}$	
Racemic Mixture	0.65	3.54	5.4	
R-isomer	0.46	12.72	27.7	
Racemic Mixture	1.26	11.25	8.9	
R-isomer	0.59	8.62	14.6	

It can be seen from Table 1 that the R-isomer of methyl [4-(2,4-dichlorophenoxy)phenoxy]propionate is significantly more active against oats than is the racemic mixture. Moreover, the R-isomer has a very greatly improved selectivity between oats and barley.

EXAMPLE 4

30 Selective herbicidal activity

The test active ingredients in this Example were the racemic mixtures and R(+) isomers of:
methyl 2-(4-[2,4-dichlorophenoxy]phenoxy)propionate (Compound 1)
isobutyl 2-(4-[4-chlorophenoxy]phenoxy)propionate (Compound 2)

The test ingredients were made up into emulsifiable concentrates as in Example 3. Dosages applied were:

35 Wheat : racemate, 2.87 Kg/hectare

isomer, 1.43 Kg/hectare

Wild oat, *Avena fatua* : racemate, 1.77 Kg/hectare

isomer, 0.89 Kg/hectare

3 replicates were used at each dosage. After 8, 14 and 28 days the mean phytotoxicity to the plants was recorded. The results are presented in Table 2.

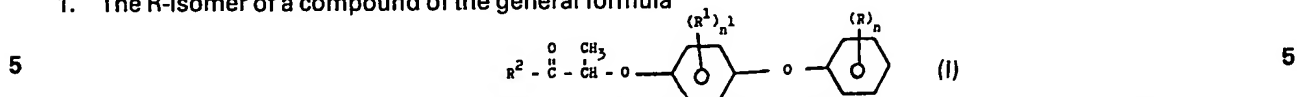
TABLE 2

Compound Tested	Wheat				Wild Oats			
	8 days	14 days	28 days	Mean	8 days	14 days	28 days	Mean
Compound 1	33	41	36	37	60	69	77	69
35 Racemic Mixture								
Compound 1	15	17	17	16	52	67	73	64
50 R-isomer								
Compound 2	21	21	24	22	30	32	30	31
55 Racemic Mixture								
Compound 2	9	16	4	10	38	37	39	38
60 R-isomer								

The results clearly show the improved selectivity of the R isomer of each compound compared with the racemic mixture.

CLAIMS

1. The R-isomer of a compound of the general formula



in which n represents 0 or an integer of 1 to 3; n¹ represents 0 or an integer of 1 to 3; each R independently represents a halogen atom, a methoxy group or an alkyl group having 1 to 4 carbon atoms; each R¹ independently represents a halogen atom or a methyl group; and R² represents a group of the general
10 formula OR³, SR⁴, NHR⁵ or NR⁶R⁷, in which R³ represents one equivalent of a salt-forming cation, a hydrogen atom, an alkyl group having from 1 to 10 carbon atoms, a trichloroethyl group, an alkenyl group having from 2 to 4 carbon atoms, a cyclohexyl group optionally substituted by one or more methyl groups, a cyclopentyl group, a phenyl group optionally substituted by one or two halogen atoms, or a benzyl group; R⁴ represents
15 an alkyl group having from 1 to 6 carbon atoms, a phenyl group optionally substituted by one or two halogen atoms, or a benzyl group; R⁵ represents a hydrogen atom, an alkyl group having from 1 to 4 carbon atoms, a phenyl group optionally substituted by one or more substituents selected from halogen atoms and -CF₃, -OCF₂CF₂H and -CO₂CH₃ groups, or a benzyl group; R⁶ represents an alkyl group having from 1 to 4 carbon atoms; and R⁷ represents an alkyl or alkoxy group having from 1 to 4 carbon atoms.

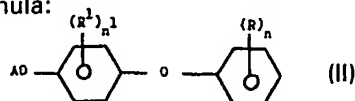
2. A isomer as claimed in Claim 1, in which n¹ represents 0, n represents 1 or 2 and the or each R
20 represents a halogen atom.

3. An isomer as claimed in either Claim 1 or Claim 2, in which R² represents a group of formula OR³ wherein R³ represents an alkyl group.

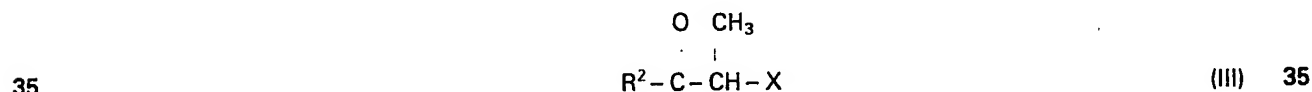
4. R-(methyl 2-[4-(2,4-dichlorophenoxy)phenoxy]propionate).

5. R-(isobutyl 2-[4-(4-chlorophenoxy)phenoxy]propionate).

25 6. A process for the preparation of a compound as claimed in any one of Claims 1 to 5, which comprises reacting a compound of the general formula:



30 wherein R, R¹, n and n¹ have the meanings given for the general formula I, and A represents a hydrogen atom or an alkali metal ion, with the S-isomer of a compound of the general formula:



where R² has the meaning given for the general formula I and the group X is a suitable leaving group, the reaction being carried out in the presence of a base if A represents a hydrogen atom; and if desired, subsequently converting the resulting R-isomer of a compound of the general formula I into the R-isomer of
40 another compound of the general formula I by any suitable method.

7. A process as claimed in Claim 6, in which X represents a group of the general formula -O.SO₂.Q or -O.CO.Q, wherein Q is a hydrocarbonyl group; a group of the general formula -O.CH(OH).CHaI₃, wherein each Hal is a halogen atom; or a halogen atom, preferably a chlorine atom.

8. A process as claimed in Claim 7, in which X represents a methanesulphonyl group or a
45 para-toluenesulphonyl group.

9. A process as claimed in Claim 8, carried out at a temperature in the range of from 50 to 200°C.

10. A process as claimed in Claim 6, carried out substantially as described in Example 1 or Example 2 herein.

11. An isomer as claimed in Claim 1, whenever prepared by a process as claimed in any one of Claims 6
50 to 10.

12. A herbicidal composition which comprises an isomer as claimed in any one of Claims 1 to 5 and 11, together with a carrier.

13. A composition as claimed in Claim 12 which comprises at least two carriers, at least one of which is a surface-active agent.

14. A method of selectively combating grass-like weeds in cereal crops, which comprises applying to the crop area a compound as claimed in any one of Claims 1 to 5 and 11 or a composition as claimed in either
55 Claim 12 or Claim 13.

15. A method as claimed in Claim 14, in which the crop is barley.

16. A method as claimed in Claim 14, in which R-(methyl 2-[4-(2,4-dichlorophenoxy)phenoxy]propionate)
60 is applied to a crop area bearing barley.